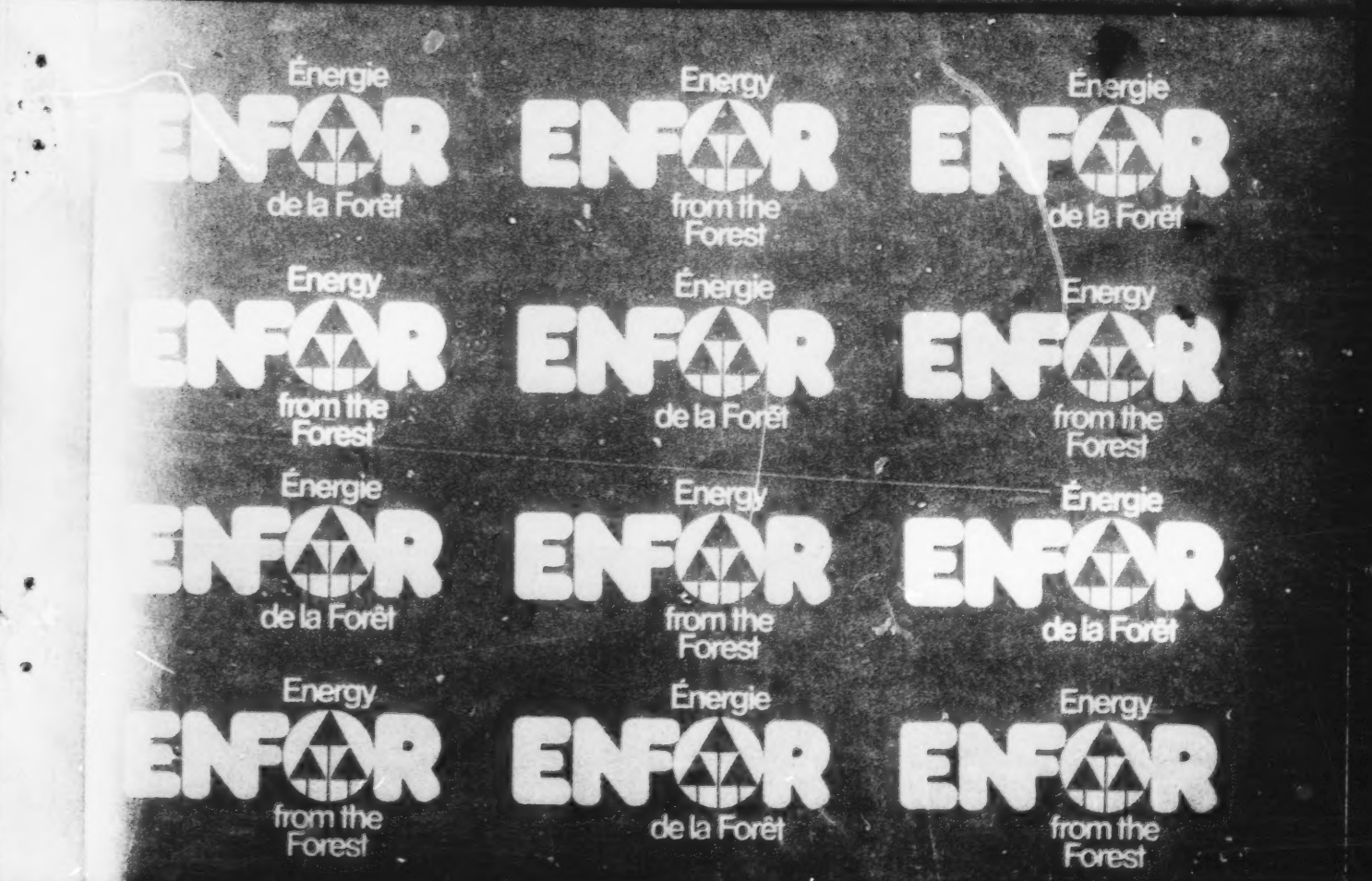
Environment Canada Environnement Canada
0050393J DEST PVM EXCH COPY 03
TP 360 E5613
VOL ISS 48 (2)
ENFOR PROJECT C

ENFOR Project C-48(2)

Production of Liquid Fuels and Chemicals From Lignocellulosic (Aspen) Materials

by

R.L. Eager, J.F. Mathews, J.M. Pepper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Contractor's Final Report [1/]
DSS Contract 41SS.KL229-1-4111

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by

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1/ This report has been reviewed by the Canadian Forestry Service and approved for distribution. Approval does not necessarily signify that the contents reflect the views and policies of the Canadian Forestry Service. Mention of trade names or commercial products does not constitute recommendation or endorsement for use.

ABSTRACT

Studies have been continued on the use of a small-scale semi-continuous reactor whereby aspen poplar wood meal may be converted into a fuel oil. Significant changes have been made in the design and operation of the unit resulting in increased throughput at lower pressures. Based on the new data consideration will be given to the design of a fully continuous reactor.

The relatively small amount of char that is formed in using the semi-continuous reactor appears to be only the result of start-up operations.

Further studies using the batch reactor have been made to evaluate the catalytic role of sodium hydroxide, lithium carbonate and cesium carbonate.

Detailed analysis of the oil obtained, by the batch process, from wood or from its separate components (cellulose and lignin) reveals a marked similarity of products. From these oils several alkanes, alkyl-substituted phenols and alkyl-substituted cyclopentanones have been isolated and identified.

TABLE OF CONTENTS

	Page
Abstract	1
Introduction	2
Research Objectives	2
Experimental Procedure and Results	3
A. Experiments using a Semi-continuous Reactor	3
a) Modifications of reaction parameters	3
b) Effect of reaction time on char formation	5
c) Effect of sodium carbonate concentration on yield of oil	5
d) Viscosity of wood oil	5
B. Experiments using the Batch Reactor	6
a) Utilization of sodium hydroxide catalyst	6
b) Utilization of lithium carbonate or cesium carbonate as catalyst	6
C. Chemical Analysis of Oils	7
Summary	8
Publications	8
Acknowledgements	9

ENFOR Project C-48(2)

Production of Liquid Fuels and Chemicals From Lignocellulosic (Aspen) Materials

This material has been presented in part at:

64th Canadian Chemical Conference, Halifax, June 1981.
58th Congress International Union of Pure and Applied Chemistry, Vancouver, August 1981.
Experts Meeting on Liquefaction, Saskatoon, February 1982.
Fourth Bioenergy R&D Seminar, Winnipeg, 1982.

INTRODUCTION

This report deals with the results of the continuation of the research conducted under ENFOR PROJECT NO C-48, DSS Contract No. OSS79 -00057 (1980-81), for which the final report was submitted in May, 1981. The conclusions made from that research and recorded in the final report are thus the basis upon which the continuing study was made. These conclusions were in part:

1. Aspen wood may be converted, in the presence of carbon monoxide, water and sodium carbonate, at elevated temperatures and pressures into a fuel oil, organic chemicals and residual carbon dioxide and hydrogen gases.

2. Water and carbon monoxide are both necessary reagents for the reaction to occur but only if Na_2CO_3 or NaOH is present.

3. There is evidence for the presence of substituted phenolic components in the oil produced from wood.

4. The water-soluble organic chemicals include aliphatic alcohols, ketones and acids containing from one to six carbon atoms.

5. Significant changes in the wood take place over a wide range of temperatures. Interactions between this set of phenomena and the shift reaction in the gaseous phase lead to the hypothesis that a temperature profile along the reactor may be preferable to constant reactor temperature.

6. Preliminary runs with the semi-continous reactor have demonstrated that the reactor can be run for extended periods and that the oil product is similar in fluidity and %(C + H) to products produced under similar conditions in previous batch reactor studies.

RESEARCH OJBECTIVES

Based on the above earlier results the research objectives to be considered under contract No OSS80-00234 were:

1. To continue the detailed study of the parameters affecting the production of an oil from aspen poplar wood using the small-scale semi-continuous reactor described in the Final Report for contract No. OSS79-00057.

2. To modify the construction of the semi-continuous reactor to improve the procedure for preparation of an oil.

3. At a time when suitable and adequate data are available to consider a tentative design for a continuously operated small-scale reactor.

4. To investigate the chemical composition of the oil obtained from both the use of batch and semi-continuous processes. The objective of this study would be to increase the understanding of the nature and mechanism of the complex chemical reactions involved and to provide information as to the nature and potential abundance of the chemicals arising by this conversion process.

5. To continue studies using the batch reactor on the nature of suitable catalysts for the conversion reaction.

EXPERIMENTAL PROCEDURE AND RESULTS

A. Experiments using a semi-continuous reactor

a) Modification of reaction parameters

Over one hundred runs have been made using the small-scale semi-continuous reactor. Parameters that have been studied include: initial and steady-state reactor pressure of carbon monoxide, temperature profiles along the reactor, auger speed (rate of wood meal delivery into the reactor zone and nominal reaction time), position of and nature of both gaseous carbon monoxide and aqueous sodium carbonate solution injections into the reactor.

A reliable procedure has been established whereby this reactor will produce a product commensurate in yield and quality with the best product obtained in earlier batch work but under conditions that are much more attractive for commercial exploitation.

Figure 1 illustrates the significant modifications that have been made to the semi-continuous reactor. The aqueous solution of catalyst (Na_2CO_3) is now pumped directly into the reactor under pressure at a

point on the reactor where the temperature has been raised to 360°C. To do this a high pressure liquid pump was installed and the rate of flow of the sodium carbonate solution controlled. In this way, the wood is introduced as air-dried meal. This has an advantage over the previously used wood meal slurry in respect of the ease of introduction by the auger. The carbon monoxide inlet was changed from the original position immediately after the wood hopper to a point located 17.8 cm downstream from the aqueous solution injection point. This permits the continual addition, under pressure, of carbon monoxide into the reactor during a run. The carbon monoxide is pumped from a storage cylinder, originally at 34.5 MPa (5000 psi), at a rate such that every five minutes approximately 0.14 MPa (20 psi), determined by difference, is introduced into the reactor. The oil and water collectors are installed such that the lower aqueous phase can be removed periodically and the pressure on the system regulated by a release valve to atmosphere. Pressure transducers were installed to record pressures in the hopper and near the end of the reactor zone. Under these conditions it was found that a wood meal "plug" was formed in the reactor just prior to the aqueous carbonate injection port (Figure 1). At steady state conditions the "plug" remained even though the wood meal was continuously being fed into the reactor and converted to oil and water-soluble products.

The experimental conditions and a description of the products obtained from several significant runs are given in Table 1.

b. Effect of reaction time on char formation

It may be seen that in all runs a char fraction is obtained which is found at the exit end of the reactor tube. Previous experiments had shown that this material could not be subsequently converted to an oil and hence it would appear to be a product resulting directly from the wood. A series of runs was made at different times of reaction (hence different amounts of wood meal admitted) to determine if the char formation was unrelated to the amount of wood and only associated with the start-up conditions. These results are given in Table 2.

The relatively small amount of char that is formed appears to be the result of start-up operations. Once a steady-state has been achieved in the reactor there is no evidence of further char build up and hence disposal of the char would not become a problem in continuous operation.

c. Effect of sodium carbonate concentration on yield of oil

A series of runs was also made to study the effect of sodium carbonate concentration. These results are given in Table 3. The presence of sodium carbonate appears to be necessary to prevent char formation, however a satisfactory product is obtained when as little as 1.25% (on a dry wood basis) is used.

d. Viscosity of wood oil

A Haake concentric cylinder viscometer was used to study some of the properties of the oil obtained from Run 113 (see Table 2). The

oil was very viscous and the instrument was limited in use to low shear rate ranges. The results are given below.

Temperature (°C)	Viscosity* (poise)	Shear rate (rpm)
50.3	66.7	0.1- 1.41
65.5	3.9	0.1-25.6
80.3	0.47-1.38	2-256

*An average viscosity value for each temperature, except for 80.3°C where a range is indicated.

The viscosity decreases rapidly with increased temperature. These results indicate that the oil is non-Newtonian in behaviour and that its viscosity is very time dependent in that at constant speed the viscosity decreases with increasingly longer times of operation.

B. Experiments using the batch reactor

a) Utilization of sodium hydroxide catalyst

Using the batch reactor a series of runs was made to study the feasibility of replacing sodium carbonate by sodium hydroxide as the alkaline catalyst. The results are given in Table 4.

The use of sodium hydroxide results in a slightly lower yield. The oil appears to be less viscous, and slightly different in colour.

b) Utilization of lithium carbonate or cesium carbonate as catalysts

Lithium and cesium carbonates were used to study the influence of the cation as part of the catalytic action for the conversion of aspen wood to an oil. The results are given in Table 5.

The salt Li_2CO_3 was not completely soluble at the concentrations used.

The use of lithium and cesium carbonates appear to result in a slightly lower yield and CHR. The oils formed using Li_2CO_3 and Na_2CO_3 were black and moderately viscous while those resulting from the use of Cs_2CO_3 were more fluid and had a slight reddish tinge.

C. Chemical Analysis of Oil

A study of the chemical composition of the oil has been continued in the belief that such knowledge would be useful in future studies on the optimum conditions for its preparation, on potential methods of upgrading the oil to a more useful fuel and on direct utilization of some products as commercially useful chemicals.

To simplify the study oils obtained using separate samples of the wood components cellulose and lignin were also studied.

A useful chemical separation was achieved by the direct extraction of the acidic (mainly phenolic) components of the oils using 5% sodium hydroxide. Acidification of the alkaline extract, and subsequent examination, by gas chromatography-mass spectroscopy, of the isolated organic fraction, permitted the identification of several alkyl-substituted phenolic compounds. The identity of these compounds and their yields (as percentage of original oil) are given in Table 6.

Subsequently gas chromatography-mass spectroscopy analyses of the whole oils led to the identification of a series of alkyl-substituted cyclopentanones. The required reference compounds were available commercially or were synthesized. The identity of these compounds and their yields (as percentages of the original oil) are given in Table 7.

SUMMARY

The modifications of the semi-continuous reactor have resulted in significant advances in the procedure from a point of view of future commercial design. Possibly the most important observation, and one that can be reproduced with confidence, is the ability to establish a "plug" of wood meal early in the reactor zone. This leads to a significant pressure differential between the wood hopper and the reactor zone and also prevents water flashing back from the reaction zone to the wood hopper. It has been found that the reaction zone can be maintained at the same high temperatures as used in the batch reactor system but using significantly lower pressures. At the same time it was found possible to increase the auger rotation speed and thus to decrease the time required to convert any given amount of wood. A distinct possibility arises that a fully continuous reactor may be designed to operate at lower pressures.

The isolation of alkyl-substituted phenols and cyclopentanones from the proto-oil along with the several low molecular weight aliphatic ketones, alcohols and acids, previously shown to be present in the aqeuous phase (2) suggest that such a process to produce an alternate fuel may simultaneously be a source of useful chemicals.

PUBLICATIONS

1. Richard L. Eager, Joseph F. Mathews, James M. Pepper and Hussein Zohdi, Studies on the Products Resulting from the Conversion of Aspen Poplar to an Oil. Canadian Journal of Chemistry 59, 2191-2198 (1981).

2. R.L. Eager, J.F. Mathews and J.M. Pepper, Liquefaction of Aspen Poplar Wood. Canadian Journal of Chemical Engineering, 60, 289-294 (1982).

ACKNOWLEDGEMENTS

The assistance provided by technicians K. Thoms and V. Gummadi and the gas chromatographic-mass spectral analyses provided by L. Hogg, NRC, Saskatoon, are appreciated.

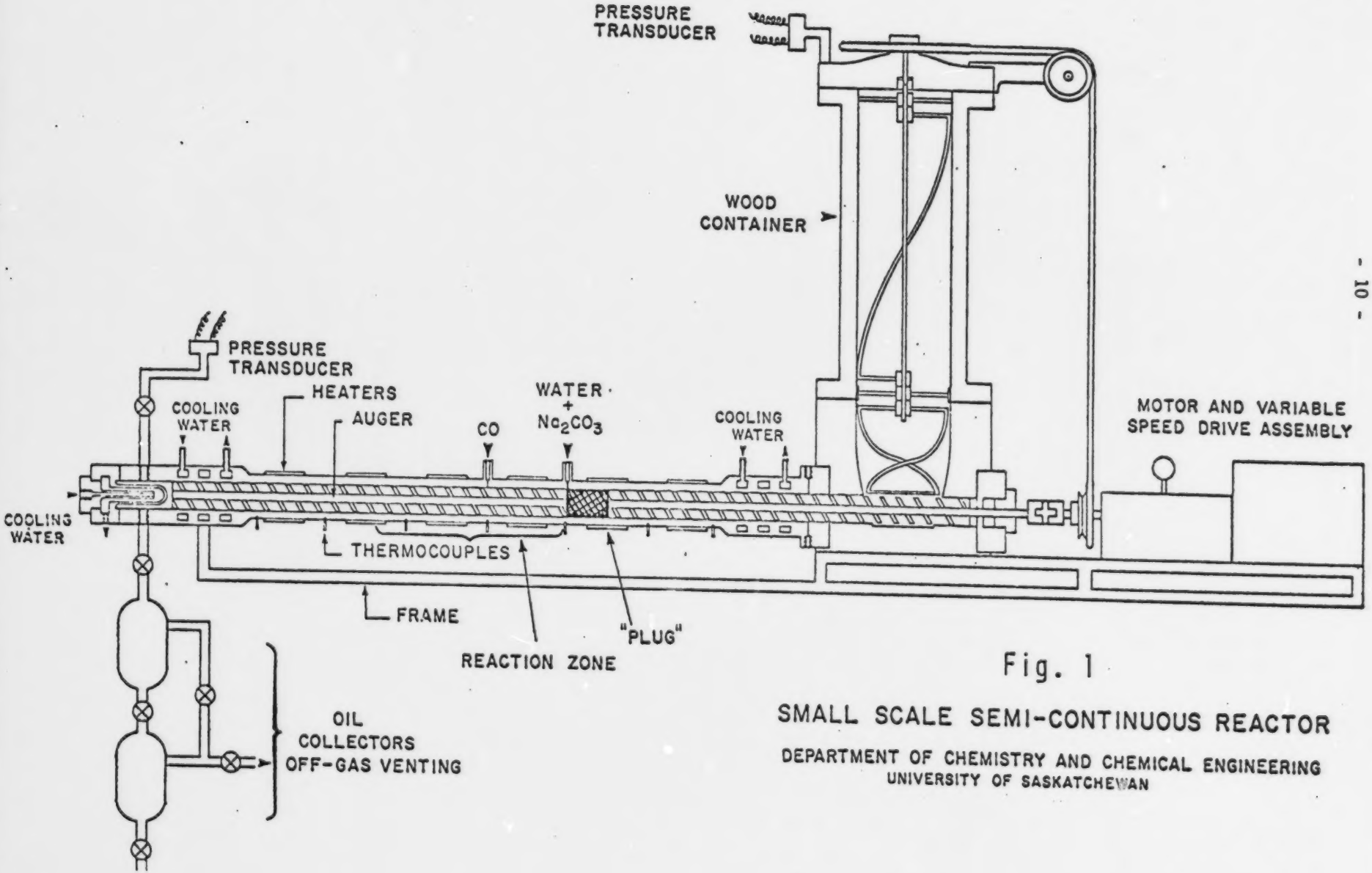

Fig. 1

SMALL SCALE SEMI-CONTINUOUS REACTOR

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF SASKATCHEWAN

TABLE 1. CONVERSION OF ASPEN WOOD[1]

RUN	GAS	PRESSURE M Pa		PRODUCT OIL			CHAR	REMARKS
		HOPPER	CONTROLLED	Yield %[3]	C, %	H, %	%[3]	
74-80[2]	CO	27.6	33.8	41	72.5	6.9	8.8	Fluid
95	CO	17.2	20.7	42	76.2	6.7	2.6	Fluid, greasy
96	N_2	17.2	20.7	41	69.5	7.0	0.8	Viscous, sticky
97	CO	17.2	20.7	44	70.2	7.2	0.7	Fluid, greasy
98	CO	13.8	17.2	42	68.2	6.7	0.8	Slightly more viscous
99	CO	10.3	13.8	36	73.2	7.2	5.9	Very viscous
100	CO	10.3	13.8	37	70.7	6.8	4.7	Moderately viscous[4]

[1] Wood meal (500 g); auger speed (12-14 rpm); Na_2CO_3 (5%) at 8 mL/min; reaction time (2.25 h); temperature (360°C).

[2] Data are averages of seven runs made to prepare sample for analysis.

[3] Percentage yield based on wood meal converted.

[4] Na_2CO_3 (5%) at 10 mL/min.

TABLE 2 EFFECT OF TIME ON CHAR FORMATION[1]

Run No	Time of Reaction (hr)	Char (g)
98	2.3	3.5
112	2.0	10.5
113	2.3	9.0
114	0.5	6.0
115	0.75	11.0

[1]Wood meal (500 g), auger speed (12 rpm); initial hopper pressure 13.8 M Pa (2000 psia); controlled reaction pressure 17.2 M Pa (2500 psia); Sodium carbonate solution (5%) introduced at 8 mL/min.

TABLE 3 EFFECT OF Na_2CO_3 CONCENTRATION[1]

RUN	Na_2CO_3 %	PRODUCT OIL				Char		REMARKS
		Yield, g	%[2]	%C	%H	Wt.g.	%[2]	
100	5.0	134	37	70.7	6.8	17	4.7	Moderately viscous oil
104	2.5	148	40	75.5	6.9	20	5.4	Moderately viscous oil
105	1.25	137	41	71.6	6.8	15[3]	4.5	Moderately viscous oil
106	0.0	104	32.5	70.1	6.5	50[4]	15.6	Viscous tar containing particles of char

[1]Wood meal (500 g); Auger speed (12-14 rpm); Initial hopper pressure of CO 10.3 M Pa (1500 psia); Controlled reactor pressure 13.8 M Pa (2000 psia); sodium carbonate solution introduced at 10 mL/min; Reaction time (2.25 h).

[2]Percentage yield based on wood meal converted.

[3]Carbon, 72.1%; hydrogen, 6.8%.

[4]Carbon, 74.4%; hydrogen, 6.2%.

Table 4 Effect of NaOH as Catalyst[1]

Initial Conditions		Oil Analysis			Oil Yield	
Temp. °C	CO pressure M Pa	%C	%H	CHR[2]	NaOH	Na_2CO_3[3]
360	5.2	69.2	8.0	29.3	38.0	40.1
320	5.2	68.8	7.6	27.9	36.5	40.7
360	8.6	73.7	8.1	30.7	37.6	41.7
320	8.6	68.9	7.6	29.2	38.1	42.8

1. Wood meal (100 g), water (250 g), Na_2CO_3(12.5 g), NaOH (9.4 g, equal sodium in concentration).

2. The carbon and hydrogen recovery (CHR) factor; defined as; [CHR = g(C+H)/g oil x (g oil/g wood) x 100].

3. Yields obtained from previous experiments made under the reaction conditions indicated but using Na_2CO_3 catalyst.

TABLE 5 EFFECT OF Li_2CO_3 AND Cs_2CO_3 AS CATALYSTS[1]

Catalyst : g		Wood, g	H_2O, g	Product oil			
				Yield, %[2]	%C	%H	CHR
Li_2CO_3	8.7	100	250	38.5	69.5	7.6	29.7
Li_2CO_3	8.7	100	250	37.7	71.8	7.2	29.8
Na_2CO_3	12.5	100	250	41.7	68.0	7.6	31.5
Cs_2CO_3	25	50	125	40.6	69.9	7.8	31.6
Cs_2CO_3	25	50	125	39.6	66.4	7.4	29.2
Na_2CO_3	3.75	50	125	44.0	69.1	7.8	33.8
Na_2CO_3	3.75	50	125	43.2	67.6	7.6	32.5

[1] Temperature, 360°C; initial CO pressure, 8.6 M Pa (1250 psia).

[2] Percentage yield based on mass of wood used.

Table 6 Isolation of Phenolic Compounds

Compound	Yields (percent of original oil)[1]		
	Wood	Cellulose	Lignin
Phenol	0.22	0.07	0.67
o-Cresol and/or 2,6-Dimethylphenol	0.12	0.10	0.17
m-or p-Cresol	0.13	0.13	0.32
2-Ethylphenol	0.05	0.06	0.11
2,4-Dimethylphenol and/or 2,5-Dimethylphenol	0.08	0.14	0.14
3-Ethylphenol and/or 4-Ethylphenol and/or 2,3-dimethylphenol	0.12	0.16	0.32
TOTALS	0.72	0.66	1.73

[1] Analyzed by gas chromatography using a 6' x 1/8" column packed with 10% SP-1200/1% H_3PO_4 on Chromosorb W (80-100 mesh) using 1 L, temperature programmed for 30°C for 4 minutes at 10°/minutes to 180° and held at 180°C; carrier gas, N_2, at 10 mL/min. Calibration curves made for each pure reference compound.

Table 7 Isolation of Substituted Cyclopentanones

Compound	Yields (percent of original oil)[1]		
	Wood	Cellulose	Lignin
2-Methylcyclopentanone	0.49	0.54	0.12
3-Methylcyclopentanone	0.18	0.28	0.08
2,5-Dimethylcyclopentanone	0.08	0.10	negligible
2,3-Dimethylcyclopentanone and/or 2,4-Dimethylcyclopentanone	0.61	0.80	0.59
2-Ethylcyclopentanone	0.34	0.41	0.12
2-Ethyl-5-Methylcyclopentanone	0.21	0.44	0.12
3-Ethyl-2-Methylcyclopentanone and/or 4-Ethyl-2-Methylcyclopentanone	0.27	0.38	0.11
2-Propylcyclopentanone	0.34	0.39	0.12
2-Methyl-5-Propylcyclopentanone	0.37	0.44	0.19
2-Butylcyclopentanone	0.40	0.32	0.12
TOTAL	3.29	4.10	1.57

[1] See footnote Table 6.

This report has been produced through an ENFOR contract

Ce rapport a été produit dans le cadre du programme ENFOR